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The use of iminopyridines as efficient ligands in the palladium(II)-catalyzed cyclization of (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates

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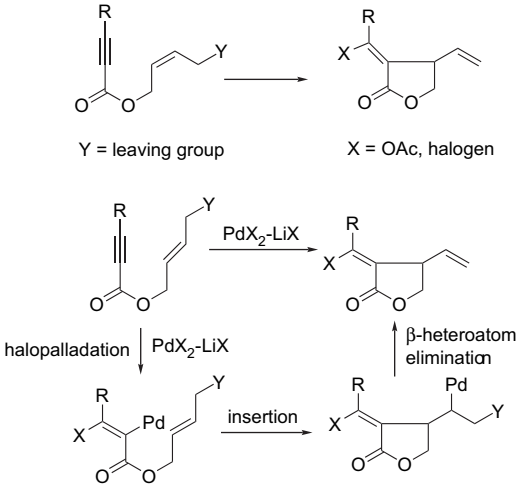
Abstract—Iminopyridines were found to be a sort of efficient bidentate ligands for the palladium(II)-catalyzed cyclization of (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates in acetic acid to afford the α-(*Z*)-acetoxyalkylidene-β-vinyl-γ-butyrolactones. The iminopyridine ligands could not only inhibit β-hydride elimination but also stabilize the vinyl-palladium intermediate in acetic acid in the reaction.

1. Introduction

The α-methylene-γ-butyrolactone ring is an integral building block of many natural products, especially the sesquiterpene lactones in which the conjugated exocyclic double bond is considered to be responsible for their interesting biological properties.[1] Since the discovery of several naturally occurring cytotoxic or antitumor agents (e.g., eupurotin, elephantin, vernolepin, etc.) that possess the α-methylene lactone ring, much interest has been shown in this class of compounds. Several reviews dealing with the synthesis of α-methylene lactones have been published.[2] Generally, the α-methylene lactones are synthesized by α-methylenation of preformed lactones, by oxidation of α-methylenecyclobutanones or β-methylenetetrahydrofuran, and from functionalized acyclic precursors.

The use of transition metal catalysts in the carbocyclization of alkenes and alkynes offers the unique means to construct a variety of synthetically important carbo- and heterocycles with high efficiency not normally accessible by traditional methods.[3] Our laboratory has developed the facile intramolecular enyne cyclization of allylic 2-alkynoates to build polysubstituted α-alkylidene-γ-butyrolactones[4] via a Pd(II) catalyst, initiated by halopalladation (Scheme 1). In these reactions, halide ions serve not only as nucleophiles but also as a ligand to inhibit the β-hydride elimination reaction.[5] However, there exist problems in the way of developing the asymmetric version of this reaction while halides are used as a ligand. To solve these problems, a new type of reaction to construct α-alkylidene-γ-butyrolactones has been developed in which the acetoxy anion served as the nucleophile and the nitrogen-containing ligands were employed to inhibit the β-hydride elimination reaction.[6] The stoichiometric reactions strongly demonstrated that the nitrogen-containing ligands, like halides, serve to favor β-heteroatom elimination over β-hydride elimination.[6b] Similar strategy was used in the cyclization of the allylic alkynamides[7] and the electron-rich 1,6-enynes.[8]



Scheme 1. Palladium(II)-catalyzed intramolecular cyclization of allylic 2-alkynoates to yield α-alkylidene-γ-butyrolactones.

The asymmetric version of this acetoxypalladation initiated enyne-coupling reaction was achieved while chiral nitrogen-containing ligands were employed.[6a,7,8] While only

Keywords: Iminopyridines; β-Hydride elimination; β-Heteroatom elimination; Palladium(II)-catalyzed reactions; α-Alkylidene-γ-lactones.
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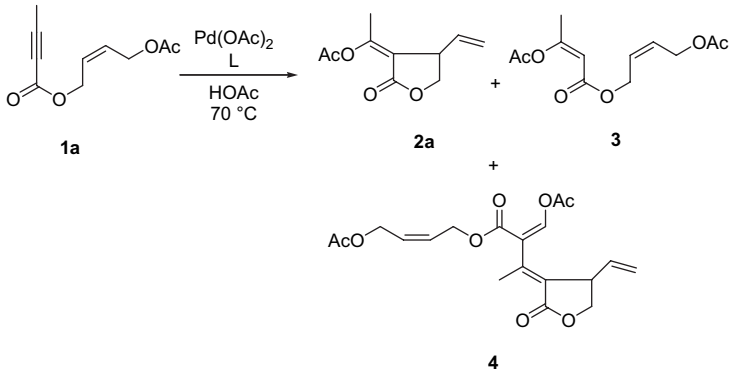
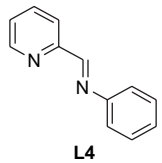
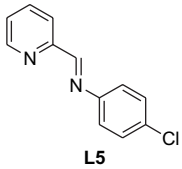
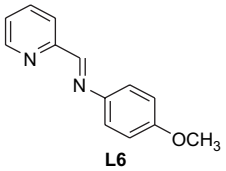
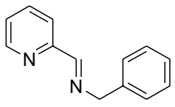
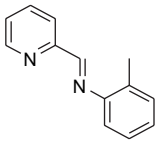
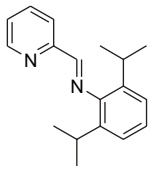
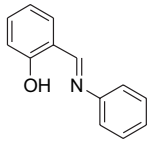
Table 1. $Pd(OAc)_2$-catalyzed cyclization of (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates[a]

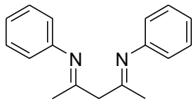
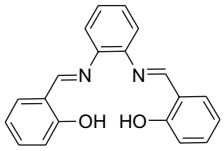
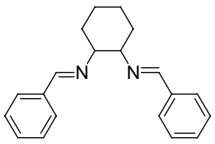
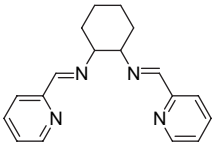


1a **2a** **3** **4**

Entry	L	Yield (%)		
		2a[b,c]	**3**	**4**
1	 **L4**	82		
2	 **L5**	71		17
3	 **L6**	73		27
4	 **L7**	80		
5	 **L8**	43	21	15
6	 **L9**	6	73	
7	 **L10**		78	

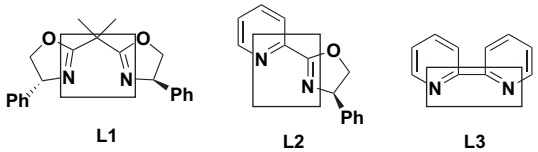
(*continued*)

Table 1. (*continued*)

Entry	L	Yield (%)		
		2a[b,c]	**3**	**4**
8	 **L11**	9	63	
9	 **L12**		73	
10	 **L13**	20	61	
11	 **L14**	17	69	

[a] Reaction conditions: **1** (0.5 mmol), $Pd(OAc)_2$ (0.027 mmol), and L (0.04 mmol) in HOAc (2.0 mL) at 60 °C.
[b] Isolated yield.
[c] The stereochemistry of the exocyclic double bond in **2a** was assigned as (*Z*)-configuration based on the higher field chemical shift of the methyl group in ^{1}H NMR spectra for the *Z* isomer.[13]

two nitrogen-containing ligands (**L1** and **L2**, Scheme 2) showed excellent results in the asymmetric cyclization of enyne (up to 92% ee),[6a] most of the test ligands gave only moderate yield and enantioselectivity.[6–8] It is therefore still worth studying the other kinds of ligands for this reaction. Here, we wish to report the results of using diimines as the ligands for this reaction and the use of iminopyridines as the efficient ligands for the non-asymmetric version of this reaction.



Scheme 2. Efficient ligands for the cyclization of (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates under Pd(II) catalysis.[6a–c]

2. Results and discussion

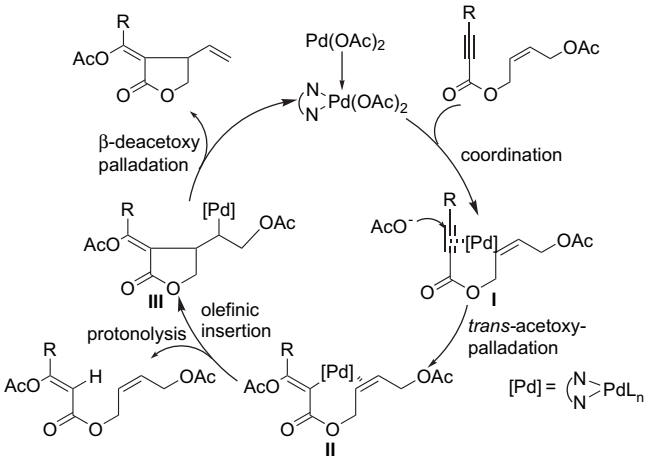
In our previous work, we tried many nitrogen-containing ligands. It was shown that a diimino structure existed in the nitrogen ligands have been proved to be efficient for the palladium(II)-catalyzed enyne cyclization (Scheme 2).[6–8] Diimine ligands have received increasing attention recently due to their special coordination behavior associated with tunable steric and electronic properties. A number of metal complexes of diimines have been reported in various reactions.[9] A lot of works have proved that palladium complexes are excellent polymerization catalysts.[9c,10] There are also some papers revealing that palladium complexes with diimine ligands are highly efficient catalysts for Suzuki cross-coupling and Heck reactions.[11] It occurred to us that the enyne cyclization might be attained through the use of palladium catalysts with diimine ligands.

2.1. Screening of the diimine ligands

As indicated in literatures,[12] an attractive characteristic of diimine lies in its flexible alterability of structure, which leads to different steric and electronic properties. Any fine-tuned imine may show different catalytic activity in the reaction. In order to investigate which structure of diimine is effective in the palladium-catalyzed enyne cyclization reaction, we first screened different diimines as the ligands using a model reaction. Compound **1a** was used as the substrate, which was reacted in the presence of $Pd(OAc)_2$ (10 mol %) and the ligand (20 mol %) in HOAc at 60 °C. The result is shown in Table 1.

Three products were observed under different diimine ligands. Besides the main product of cyclization, α-(*Z*)-(1′-acetoxyethylidene)-β-vinyl-γ-butyrolactone (**2a**), the protonolysis product of the vinylic palladium species (**3**)

was also observed in the reaction in many cases. As shown in the proposed mechanism in Scheme 3, there is a competition between insertion of the olefin into the vinyl-palladium intermediate **II** and protonolysis of the vinyl-palladium intermediate **II** formed by trans-acetoxypalladation of the carbon–carbon triple bond. As we know, vinyl-palladium intermediate **II** was readily protonized in HOAc media. Therefore, the role of an efficient ligand should not only inhibit β-hydride elimination but also stabilize the intermediate **II** in acetic acid to make intramolecular olefinic insertion possible. Obviously, some iminopyridines (Table 1, entries 1–4) could play this role successfully. The formation of a two-component adduct **4** emerged as a major byproduct in some cases (Table 1, entries 2, 3, and 5) may be due to the high substrate concentration of the reaction. From our previous experience, the intermolecular reaction could be suppressed by diluting the reaction system. However, the use of *o*-substituted iminopyridines as ligands suppressed the cyclization of substrate **1a** (Table 1, entries 5 and 6). We also tried to use the compounds with more coordination sites but were all defeated (Table 1, entries 9 and 11). From these results, it is clear that pyridinyl group in the imine ligand is necessary and only bidentate iminopyridine ligands are effective in our modeled palladium-catalyzed enyne cyclization reaction.

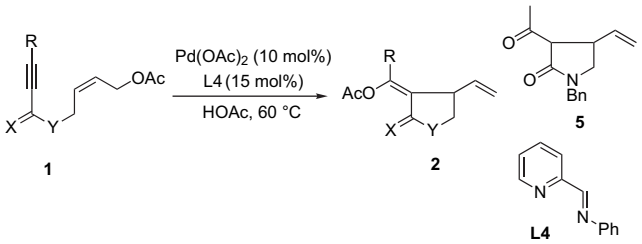


Scheme 3. Proposed mechanism of the cyclization of (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates catalyzed by $Pd(OAc)_2$/bipyridine.

2.2. Scope of the cyclization reactions of (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates

In order to study the generality of the method, other substituted alkynoates (e.g., phenyl, *n*-alkyl or methoxymethyl, etc.), electron-deficient substrates, and electron-rich substrates (e.g., alkynoates, alkynyl ether, alkynyl amine, etc.) were investigated using *N*-phenyl-2-pyridinealdimine (**L4**) as our standard ligand. The results are shown in Table 2. Both the substrates with electron-deficient triple bonds (Table 2, entries 1–6) or that with electron-rich triple bonds (Table 2, entries 7–9) reacted smoothly to give cyclization products in moderate to good yields. Furthermore, substrates containing nitrogen atom (Table 2, entries 6 and 7) gave better results. This might be explained by the fact that the nitrogen atom could also coordinate to palladium making the vinyl-palladium intermediate more stable.

Table 2. Cyclization of various (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates in the presence of *N*-phenyl-2-pyridinealdimine (**L4**)[a]



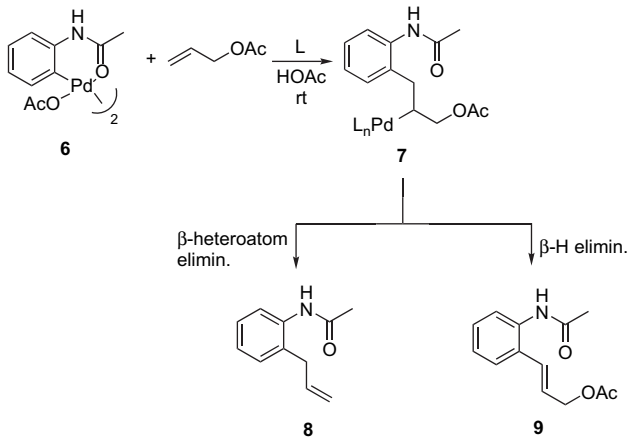
Entry	1	R	X	Y	2	Yield[a,b] (%)
1	**1a**	CH_3	O	O	**2a**	83
2	**1b**	*n*-Pr	O	O	**2b**	81
3	**1c**	Ph	O	O	**2c**	86
4	**1d**	n-C_7H_{15}	O	O	**2d**	76
5	**1e**	CH_3OCH_2	O	O	**2e**	74
6	**1f**	CH_3	O	NBn	**2f**	63[c]
7	**1g**	CH_3	H_2	NTs	**2g**	88
8	**1h**	CH_3	H_2	O	**2h**	51
9	**1i**	CH_3	H_2	$C(COOMe)_2$	**2i**	69

[a] Reaction conditions: $Pd(OAc)_2$ (10 mol %), **L4** (15 mol %), and HOAc (2 mL) at 60 °C.
[b] Isolated yield.
[c] Hydrolysis product (**5**) of the cyclization product **2f** was obtained in 33% yield.

2.3. Role of iminopyridine ligands

With these satisfactory results in hand, we are interested in studying the role of these iminopyridines (**L4–L7**, Table 1, entries 1–4). Our previous work has shown that excess of halide ions and bipyridine (bpy) ligand can block the usual β-hydride elimination,[5,6] and this role has been confirmed by a stoichiometric reaction of the palladium complex **6** with allyl acetate in the presence of different ligands including halides and the nitrogen ligands. In the above catalytic cycle of the cyclization of (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates, the normal β-hydride elimination of intermediate **III** (Scheme 3) was also inhibited and β-acetoxy elimination took place instead. Evidently, the iminopyridine ligands play a key role here. In order to probe the role of the iminopyridines in this reaction, a similar stoichiometric reaction of the palladium complex **6** with allyl acetates[5,6] in the presence of iminopyridines (**L4–L7**) was investigated. An intermediate **7** formed by intermolecular olefinic insertion into the aromatic carbon–palladium bond was postulated. From the intermediate **7**, β-acetoxy elimination leads to **8**, while β-hydride elimination gives **9**. The results are summarized in Table 3. From Table 3, it was shown that, like chloride ion, pyridine, bipyridine, and phenanthroline (Table 3, entries 2–5), reactions in the presence of iminopyridines (**L4–L7**) afford **8** in medium to good yield (Table 3, entries 6–9). While the same reaction was carried out in the absence of any ligand, the β-hydride elimination product **9** was isolated in 66% yield. Evidently, iminopyridines were also effective ligands for inhibiting β-hydride elimination in the cyclization reaction of (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates. Similar to the role of halide ions and bipyridine ligand, this might be ascribed to the following: (a) the presence of iminopyridine ligands makes Pd coordinatively saturated and the β-hydride elimination not so feasible; (b) the coordination of iminopyridine ligands to Pd increases

Table 3. Stoichiometric reactions of palladium complex (**6**) with allyl acetate in the presence of different ligands[a]



Entry	L	L/Pd	Observation	Yield[b] (%)	
				8	**9**
1	None		Pd ↓		66
2	Cl^-	10/1	Clear solution	75	
3	py	2/1	Clear solution	69	
4	bpy	1/1	Clear solution	81	
5	phen	1/1	Clear solution	77	
6	L4	2/1	Clear solution	66	
7	L5	2/1	Clear solution	81	
8	L6	2/1	Clear solution	66	
9	L7	2/1	Clear solution	75	

[a] Reaction conditions: complex **6** (0.13 mmol) and allyl acetate (1.3 mmol) in HOAc (2.0 mL) at room temperature.
[b] Isolated yield based on Pd complex.

the electron density of Pd, resulting in increasing stability of the carbon–palladium bond toward protonolysis.[5,6]

3. Conclusion

In conclusion, we have demonstrated an efficient method for palladium(II)-catalyzed cyclization of (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates in acetic acid to afford the α-(*Z*)-acetoxyalkylidene-β-vinyl-γ-butyrolactones using iminopyridines as ligands. The role of iminopyridine ligands in this cyclization was studied through a stoichiometric reaction. The results show that the presence of iminopyridine ligands might inhibit the β-hydride elimination and stabilize the carbon–palladium bond to make the reaction more feasible. These results may be also usable in performing the mechanism of polymerization of alkenes using palladium(II)–iminopyridine catalysts.[10]

4. Experimental

4.1. Materials

The diimine ligands were prepared according to the literatures.[12] The known substrates, (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates, were prepared according to the reported procedure.[6b,7,8] The palladium complex **6** was prepared using the literature procedure.[14]

4.2. Preparation of (*Z*)-4′-acetoxy-2′-butenyl 2-decynoates (1d)

To a solution of 2-decynoic acid (3.36 g, 20 mmol) and (*Z*)-1-acetoxy-2-buten-4-ol (2.86 g, 22 mmol) in CH_2Cl_2 (20 mL) was added dropwise at −20 °C a solution of 1,3-dicyclohexylcarbodiimide (4.13 g, 20 mmol) and 4-(dimethylamino)pyridine (224 mg, 2 mmol) in CH_2Cl_2 (20 mL) with stirring. Then the reaction mixture was stirred at room temperature for 10 h. After the reaction was complete, the white solid was filtered off and the solvent was removed in vacuo. The residue was then subjected to column chromatography on silica gel (petroleum ether–ethyl acetate 5:1), affording **1d** as an oil. IR (neat): *ν* 2932, 2238, 1744, 1713, 1373, 1242, 1072 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): *δ* 5.80–5.76 (m, 2H), 4.76 (d, *J*=5.4 Hz, 2H), 4.68 (d, *J*=4.8 Hz, 2H), 2.35 (t, *J*=7.2 Hz, 2H), 2.07 (s, 3H), 1.63–1.53 (m, 2H), 1.28–1.42 (m, 8H), 0.88 (t, *J*=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 170.6, 153.3, 128.6, 127.0, 90.2, 72.6, 60.9, 59.8, 31.5, 28.6, 28.5, 27.3, 22.4, 20.7, 18.5, 13.9. MS (*m/z*): 279 (M^+-1), 151 (100), 81. HRMS: calcd for $C_{16}H_{24}O_4Na^{+1}$ 303.1571, found 303.1567.

4.3. Typical procedure for the cyclization of (*Z*)-4′-acetoxy-2′-butenyl 2-alkynoates: synthesis of α-(*Z*)-(1′-acetoxyoctylidene)-β-vinyl-γ-butyrolactone (2d)

To a solution of $Pd(OAc)_2$ (6 mg, 0.027 mmol) and iminopyridine ligand **L4** (7.3 mg, 0.04 mmol) in HOAc (2 mL) at 60 °C was added **1d** (140 mg, 0.5 mmol) with stirring. After the reaction was complete as monitored by TLC, ethyl ether (80 mL) was added. The mixture was washed with saturated $NaHCO_3$ solution (2×20 mL) and brine (20 mL). The ether layer was dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was subjected to column chromatography on silica gel (petroleum ether–ethyl acetate 4:1), affording pure **2d** as an oil. IR (neat): *ν* 2932, 1760, 1675, 1374, 1212, 1157 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 5.88–5.80 (m, 1H), 5.28–5.19 (m, 2H), 4.43 (dd, *J*=8.8, 8.4 Hz, 1H), 4.04 (dd, *J*=9.2, 3.2 Hz, 1H), 3.79–3.75 (m, 1H), 2.30 (t, *J*=8.1 Hz, 2H), 2.27 (s, 3H), 1.50–1.48 (m, 2H), 1.34–1.14 (m, 8H), 0.88 (t, *J*=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 168.2, 167.5, 160.2, 136.2, 117.3, 114.2, 69.8, 42.0, 33.2, 31.6, 29.3, 28.9, 25.5, 22.5, 20.8, 14.0. MS (*m/z*): 280 (M^+), 238, 154, 136 (100), 109, 95, 57. HRMS: calcd for $C_{16}H_{24}O_4Na^{+1}$ 303.1563, found 303.1567.

4.4. General procedure for the stoichiometric reactions of di-μ-acetatobis(2-acetaminophenyl-2C,O)dipalladium(II) (6) with allyl acetate in the presence of different ligands

To a suspension of complex **6** (80 mg, 0.13 mmol) and the corresponding ligand in HOAc (1 mL) was added allyl acetate (135 mg, 1.35 mmol). The mixture was stirred at room temperature for 1.5 h. After separation of palladium by filtration through a short column of silica gel with the aid of ethyl acetate, the filtrate was concentrated under vacuum and the residue was subjected to column chromatography on silica gel (petroleum ether–ethyl acetate 2:1) to afford products **8** or **9** as shown in Table 3.

4.4.1. *N*-Acetyl-2-allylaniline (8).[5] IR (KBr): ν 3286, 1657, 1587, 1536, 1482, 1371, 1298, 994, 970, 916, 753 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, J=8.0 Hz, 1H), 7.29–7.09 (m, 4H), 6.01–5.92 (m, 1H), 5.20–5.06 (m, 2H), 3.39 (d, J=6.0 Hz, 2H), 2.15 (s, 3H). MS (*m*/*z*): 176 (M^++1), 175 (M^+), 160, 132 (100), 118, 91, 77.

4.4.2. *N*-Acetyl-2-(3-acetoxy-1-propenyl)aniline (9).[5] IR (KBr): ν 3240, 1736, 1652, 1579, 1542, 1455, 1301, 1239, 1025 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J=8.1 Hz, 1H), 7.41–7.13 (m, 4H), 6.76 (d, J=15.6 Hz, 1H), 6.22 (m, 1H), 4.76 (dd, J=6.3, 1.6 Hz, 2H), 2.22 (s, 3H), 2.12 (s, 3H). MS (*m*/*z*): 233 (M^+), 191, 173, 130 (100), 118, 77, 43.

Acknowledgements

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Supplementary data

Characterization data of the substrates, products, and copies of the ^1H NMR spectra of the compounds **1d**, **2d**, and products of the stoichiometric reaction, **8** and **9** are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.04.006.

References and notes

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